REMARKS

Claims 1-20 are presently pending. In the July 22, 2004 Final Office Action, the Examiner largely repeated the rejections of the February 13, 2004 Office Action. The Examiner:

1. Rejected claims 1, 3-6 as anticipated under 35 U.S.C. § 102(b) by Bell (U.S. Patent No. 5,463,191);
2. Rejected claim 2 as obvious under 35 U.S.C. § 103(a) over Bell in view of Yokono (U.S. Patent No. 5,150,005);
3. Rejected claim 8 as obvious over Bell in view of Curcio (U.S. Patent No. 6,452,117);
4. Rejected claims 9-20 as obvious over Bell in view of Stevens (U.S. Patent No. 6,392,356) in view of Nakazawa (U.S. Patent No. 6,411,349) and further in view of Curcio; and
5. Allowed claim 7.

Applicants respectfully traverse.

Applicants had argued in response to the February 13, 2004 Office Action that Bell does not teach "a glass substrate" as recited in independent claim 1. Bell only teaches a fiberglass substrate. *See* Bell, 4:61-64. Applicants had further emphasized that Bell does not teach that the glass substrate protects the printed circuit board, particularly from moisture. In the July 22, 2004 Final Office Action, the Examiner disagreed stating that "the Examiner indicates that the glass fiber and polymer substrate as taught by the prior art is conventionally construed as being a 'glass substrate.'" *See* Final Office Action, pg. 10.

Applicants respectfully submit that a "fiberglass substrate" as taught in the prior art is not a 'glass substrate' as recited in the pending claims. Specifically, a fiberglass substrate is not as effective as a moisture barrier as a glass substrate. Applicants have attached an article entitled "Evaluating High Performance Diffusion Barriers: the Calcium Test," Nisato, Bouten, Slikkerveer, Bennett, Graff, Rutherford, Wiese, Asia Display, IDW/'01, pg. 1435-1438 ("Nisato Article"), which compares the WVTR (water vapor transmission rate) of glass with that of plastic. Nisato shows that the WVTR of glass is 1000-10000 times better than the WVTR of plastic. Nisato at 1436. Although fiberglass contains glass in addition to plastic, a glass substrate is still a far more effective moisture barrier than fiberglass because fiberglass permits moisture transfer through the plastic. Accordingly, Bell does not anticipate or render obvious any of the pending claims because it does not teach the 'glass substrate' limitation.

Applicants note that Bell is used as a reference in each of the Examiner's rejections. Therefore, claims 1-20 are all in condition for allowance. Favorable reconsideration is respectfully requested.

Respectfully submitted,

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Evaluating High Performance Diffusion Barriers: the Calcium Test

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ABSTRACT

In order to evaluate flexible plastic substrates for OLED applications, a permeation measurement method was developed. Based on the corrosion of reactive metal films and modeling thereof, this method is used to quantify the water transmission rate of substrates provided with high-performance diffusion barriers, including hybrid multi-layers.

INTRODUCTION

Polymer/Organic electroluminescent light emitting displays (OLED) are an interesting option for flexible displays [1]. However, organic electroluminescent (EL) materials are easily degraded by water and oxygen. In addition, the thin cathodes of these devices consist of reactive metals that degrade even more rapidly than the organic EL material. OLED displays require, therefore, substrates and sealants extremely impermeable to water and oxygen [2]. The current specifications for permeation rates of substrates for OLED are on the order of 10^{-3} cm^3/m^2/day at standard temperature and pressure for oxygen and 10^{-6} g/m^2/day for water vapor, respectively. New diffusion barrier materials and substrates based on vacuum polymer deposition [3] are a promising option for transparent, flexible substrates for OLED applications. Their encapsulation properties cannot be quantified with current permeation measurement equipment, which is limited to $5x10^{-3}$ cm^3/m^2/day for O_2 and $5x10^{-3}$ g/m^2/day for H_2O. Moreover, these permeation methods are often inconvenient for materials evaluation and development due to the time required for measurement and their inability to distinguish permeation through many sub-micron pores versus a few larger defects. There is obviously a need for new characterization methods that will allow for more sensitive and rapid assessment of barrier properties. Ultimately, a standard method to compare different substrates and materials is needed.

PRINCIPLE

The method is based on the corrosion of thin calcium films. These films, deposited on the substrate of choice, are encapsulated with a transparent adhesive/sealant and a glass lid. The calcium layer is initially a highly reflecting metallic mirror. As water and oxygen penetrate the test cell, metallic calcium reacts with oxygen and water, resulting in an increasingly transparent layer of calcium salt. [4]. The test specimens are subjected to environmental aging at a fixed temperature and humidity. Pictures of the test cells are taken at regular intervals to follow the evolution of the samples. This paper presents results obtained using two complementary test cell fabrication and data analysis methods.

TEST METHOD A

Test Cell Fabrication

Calcium layers are deposited on the plastic substrates through a shadow mask. The deposition system is installed in a glove box. A glue line is dispensed on glass lids and the calcium test cells are subsequently assembled in the glove box (Figure 1).

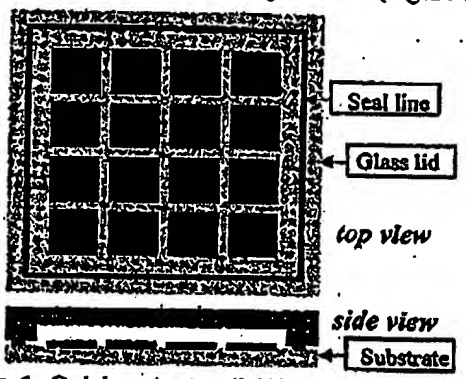

Figure 1. Calcium test cell (A): a thin calcium film deposited on a substrate encapsulated with a glue line seal and glass lid.

Measurement Setup

The detection system consists of an optical rail provided with a homogeneous light source, a sample holder and a CCD camera. Transmission photographs of calcium test cells are shown in Figure2.

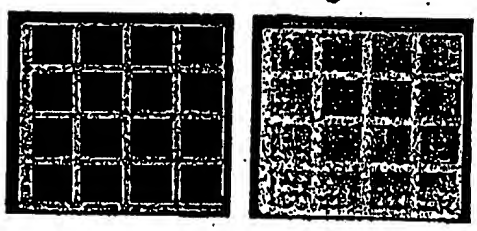

Figure 2. Example of evolution of calcium test cells. The calcium square patterns are 6 mm wide.

Automated image analysis of the photographs is performed with standard imaging software, yielding the distribution of optical transmission of the calcium layer.

Data Analysis

Method A aims at quantifying the overall corrosion of the calcium layer. Pictures of the samples are acquired as a function of time to ascertain the degradation of the cells. Optical modeling of the transmission of calcium-calcium salt stacks enables the determination of the distribution of metallic calcium thickness in the cell [5]. The latter can then be related to the amount of absorbed water as a function of time, based on the working assumption that only water contributes to the degradation of the calcium layer. A typical example of a calcium thickness histogram is shown in Figure 3.

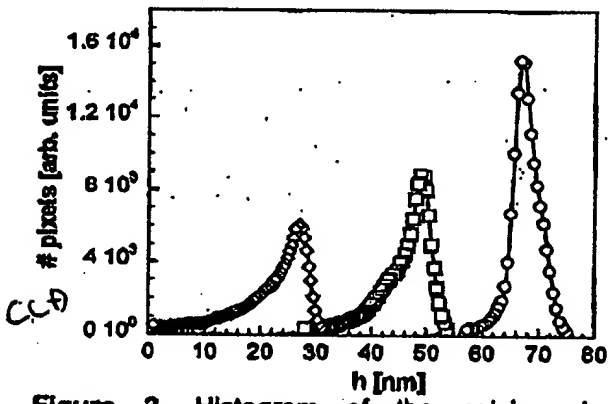

Figure 3. Histogram of the calcium layer thickness after deposition (o); after 2 days (o) and 4 days (◊). LCD grade substrate (PL2).

Results

Permeation data from several flexible substrates was obtained, namely two LCD grade plastic substrates (PL1 and PL2) provided with single layer inorganic and hybrid diffusion barriers and a Flexible Glass 500 (OLED grade) engineered substrate from Vitex Systems, comprising a plastic film with a hybrid, multi-layer diffusion barrier. Glass plates were also tested, providing data on seal lines as well as a baseline for the detection limit on the plastic substrates.

The effective water vapor transmission rates (WVTR) of the substrate or sealant [6] is obtained by fitting a straight line to the (effective) water uptake versus time curves, shown in Figure 4. Note that these are "effective" WVTR: this method does not discriminate between calcium oxide or calcium hydroxide.

The data in Table 1 shows the large differences of the transmission rates of different substrates. With the current seal line, Flexible Glass and glass substrates are almost indistinguishable. This indicates that the permeability of the seal line is the major limiting factor for this test as far as these substrates are concerned.

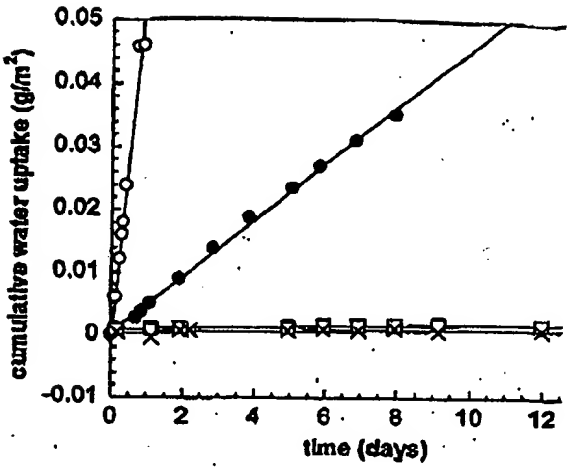

Figure 4. Example of transmission rate plot PL 1 (o); PL 2 (•), Vitex Flexible Glass (□) glass substrates (x). Solid lines are linear le squares fits to the data.

Sample	Effective WVTR [g/m²/day]
PL 1	10.10^{-1}
PL 2	7.10^{-3}
Flexible Glass 500	8.10^{-5}
Glass	5.10^{-5}

Table 1. Effective WVTR rates at 21°C and RH determined by Method A. The glass sam used as a reference (seal line permeation).

Transmission rates in the range of 10^{-1} to H_2O/m^2/day have been determined using this me Extension to a detection limit of 10^{-6} g H_2O/m^2 important for OLED applications, can be expected

While determination of the effective WVT useful, it may not be a sufficient means characterizing high performance barriers. For barriers, permeation through defects is likel dominate [7]. Therefore, failure of a display d built on these barrier substrates will be controlle how rapidly defective spots grow. Method B is l on detection of these defects and their growth time.

TEST METHOD B

Test Cell Fabrication

In method B, no glovebox is used. The cal pattern is deposited on the substrates in a va chamber and is protected by subsequent depositi the same chamber, of an unpatterned inert metal l The coated test substrates can then be removed atmosphere and encapsulated with a UV cu adhesive overcoat and glass lid (Figure 5).

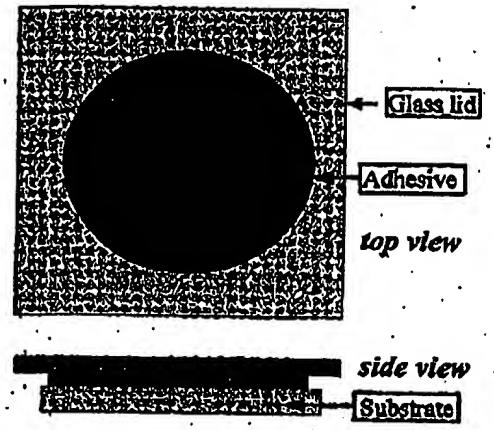

Figure 5. Test cell (B): metallic stack encapsulated with adhesive face seal and glass lid.

Measurement Setup

A microscope fitted with a CCD camera is used in the reflectance mode to monitor calcium corrosion. A 1.5 mm x 1.5 mm reticle (0.5 mm squares) is placed on the plastic substrate over the center of the calcium dot to register the photograph position. The protective metal backing on the back of the plastic substrate provides good contrast between silvery calcium and transparent calcium salt. Barrier defects (cracks, pinholes etc.) are reproduced as discrete corrosion images in the calcium film. Image analysis is used to quantify the areas converted to calcium salt.

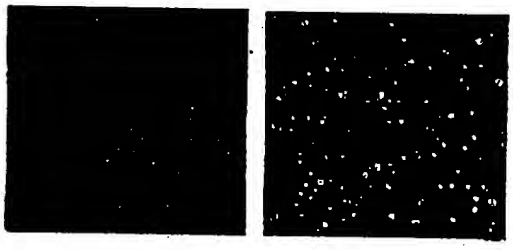

Figure 7. Example of evolution of calcium test cells at 50x magnification. Each grid square is 0.5 mm wide.

Data Analysis

A selected number of these defects are monitored at 200x magnification, while the total numbers of defects are monitored at 50x magnification. The area of individual defects, determined by image analysis, is plotted as a function of time and growth rates are analyzed. Growth rates can be used to identify and characterize the fastest growing defects and either eliminate them through further development, or estimate time to failure based on a specific set of failure criteria.

This method can also be used to calculate effective WVTR. After aging, the total area of calcium salt in a 50x image is divided by the total area of the image to get the percent calcium salt area. Working assumptions are 1) the observed defects represent conversion of the total calcium film thickness (the calcium film is thin compared to the diameter of defects), and 2) the rate of water vapor molecular flux through the barrier film is constant over the time interval. Calculations for a number of identical samples are averaged.

Results

Data from two different barrier substrates (single layer inorganic, and Vitex hybrid multi-layer) was obtained. Cells fabricated from two glass plates were also tested as controls. Because of the high barrier properties, Vitex engineered substrates were tested at 85°C and 50% RH accelerated conditions.

A number of growth curves are plotted in Figure 6 to show that different defects exhibit different growth rates depending on their origin or cause. The slope and shape of the growth curve has a dramatic effect on life time estimates, with a linear fit of the data projecting greater than 2000 hours before the largest defect reaches 100um at 85C, 50% RH.

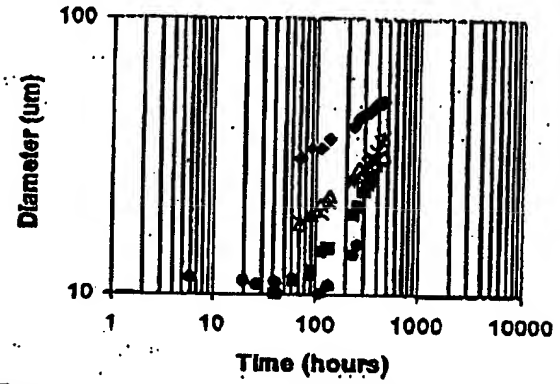

Figure 6. Five calcium salt defect growth curves on a Vitex barrier substrate at 85°C, 50%. The log-log representation facilitates lifetime estimates based on a 100 µm diameter defect failure criteria.

Elapsed Time [hours]	$Ca(OH)_2$ coverage [%]	Effective WVTR [g/m²/day]
256	0.08	$3\ 10^{-7}$
480	0.44	$8\ 10^{-6}$

Table 2. Effective WVTR for Vitex OLED grade substrates at 85°C and 50% RH determined by Method B. Glass plate test cells showed similar permeation rates.

The effective permeation rate for the Vitex substrate at 85°C and 50% RH is reported for two different aging times in Table 2. The apparent increase in effective permeation rate at long aging times is believed to be due to moisture permeation through the adhesive seal. Evidence for moisture permeation through the face seal is illustrated in Figure 7, where a

rapid increase in the number of defects is observed between 200 and 300 hours of aging. Onset of $Ca(OH)_2$ defect formation on the glass plate controls also occurs at approximately 200 hours.

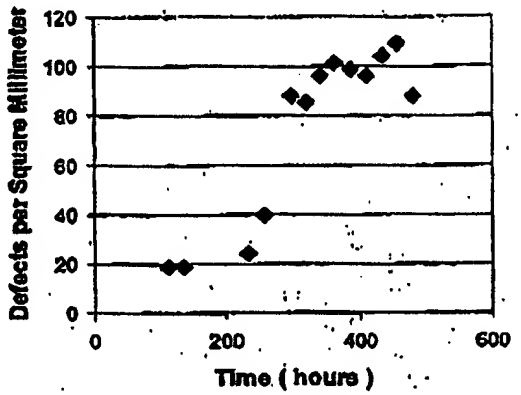

Figure 7. Defect density for Vitex barrier substrate as a function of storage time at 85°C, 50% RH.

For comparison, similar tests were carried out on LCD grade polymer substrates (PL2), however the degradation rate was too fast to obtain growth curves. Complete conversion of the calcium occurred in less than 1 hour exposure to 85°C, 50% RH.

DISCUSSION

The simple methods presented in this paper allow for an all-optical, direct comparison of the permeability of substrates, diffusion barriers and adhesive/sealants. The calcium test provides a convenient way to compare performance of different substrates. In many cases a qualitative comparative test may be sufficient. For instance, the difference between hybrid multiple and single layer barrier is remarkable. The quantification of such a method is somewhat challenging. In this regard, some of the differences between the two methods presented here highlight key issues.

Sealing. Method A relies on the robustness of a glue line seal for consistency, whereas method B uses an excess of adhesive in a face seal configuration. The added surface area for adhesion in this configuration may be important for glass to plastic sealing, especially during thermal cycling, but an adhesive that does not react readily with the calcium is required. Both methods require hermetic glues for measurement of high performance barriers. The use of glass-to-glass controls is critical for detecting limitations of the adhesive.

Exposed substrate vs. calcium coated substrate. In method A calcium does not cover the entire surface of the substrate. This allows moisture to permeate the substrate uninhibited by a calcium layer, enter the free space above the calcium and can attack the calcium from the opposite side. In method B calcium covers the entire area under test and there is no free space above the calcium. However, the transparent calci salt does not appear to act as significant diffus barrier, so either configuration should be adequate.

Data Collection. For method A quantification the degree of oxidation of the calcium layer is cruc For B obtaining adequate contrast between the calci and underlying metal is critical.

Area under Test. The substrate area under tes method A is larger than that in method B. As su method B relies on using more samples to ob representative data.

Future work is required, and will incl transmission rate calculations and comparis between optical transmission and reflective microsc as a means of detecting defects and further refinem of the adhesive and glue seal.

CONCLUSION

A calcium test is described that can effecti speed research and development on diffusion barri substrates and adhesives / sealants suitable for flex OLED devices. Two complementary methods pro quantitative results in a range inaccessible commercial equipment, potentially resulting in a fa 10^3 improvement for water vapor transmis measurements. Also provided is a powerful wa estimate the life of OLED displays based on p defect growth over time, and useful insights barrier film characteristics. Finally, results f combined application of the two methods indicates the Vitex substrates with hybrid multi-layer barrie promising for OLED applications.

ACKNOWLEDGEMENTS

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